Discussion on Isotopes.

(March 3, 1921.)

Sir J. J. THOMSON: I think I shall best open the discussion this afternoon if, instead of attempting a history of the subject of isotopes, I confine myself to a few special points. The conception of isotopes—that is, of two elements which have different atomic weights but chemical properties so closely resembling each other that they have not yet been separated by chemical methods—was, I believe, first reached by Prof. Soddy in connection with radio-active substances. In the few remarks which I have to make this afternoon, I shall not deal with these substances; I will leave them to others who are better acquainted with them than myself; I propose to confine myself to the consideration of the isotopes, or with some points connected with the isotopes, of the lighter elements.

Before doing so, I should like to say just a word about the conception of isotopes on the electron theory of an atom. On that theory the atoms of the isotopes contain an equal number of electrons. The difference in the atomic weight is supposed to be due to the simultaneous entry into the core of the atom of one or more positive charges, and an equal number of electrons, so that the electric charge on the core is not affected. In reference to this, I would like to say that it by no means follows that an electron and a positive charge will neutralise each other at the distances that occur in the atom, however close together they might be placed; and, though one would expect that the residual effect would not be large, yet I think it might easily be appreciable, and might produce some difference between the properties, chemical or physical, of the isotopes. For example, though I do not think it would affect the number of electrons in the outer layer, I think it would affect the distance of the outer layer from the core of the atom. And the statement that the chemical properties of an element depend only on the outer layer of the atom, is one with which I should agree if it is recognised that, even if the number of electrons in the outer layer is unaltered, differences in the distance of this layer from the centre may result in different chemical properties. For example, we, or at any rate some of us, believe that the valency of an element fixes the number of electrons in the outer layer. Thus, there are the same number of electrons in the outer layer of the atoms of silicon and of carbon, and yet there are well-marked differences in the chemical properties of these two substances.

With this preface, I will plunge at once into the most dramatic case of isotopes—the case of chlorine. In chlorine we have a substance with very energetic chemical properties, a substance whose atomic weight (as determined by very many observers, and with remarkably concordant results) has, I think, always been regarded as accurate to one part in a thousand, and equal to 35·5; and not only has the atomic weight of chlorine been determined by what may be called chemical methods, it has also been determined by comparing the density of the gas with the density of the standard gas, with results which were identical with those derived from chemical processes, and this fact eliminates many possible explanations which might be given for an error in the atomic weight. The position is that chemists declare the atomic weight of chlorine to be 35·5. Mr. Aston, who has measured the atomic weight of chlorine by a different method, cannot find any chlorine—or any substance—with an atomic weight of 35·5, but he does find substances with atomic weights of 35 and 37. Accepting the numbers on both sides, there does not seem to be any explanation other than that either chlorine is a mixture of these two substances of atomic weight 35 and 37, or else that, in the discharge tube which Mr. Aston employs to measure the atomic weight, some decomposition or integration—or both—of the chlorine atom has occurred.

I think the great importance of the case of chlorine is that it allows us, by an experiment of not prohibitive difficulty, to decide whether chlorine is a mixture or not, and thus settle the question of its isotopes. This is due to the fact that chlorine has such pronounced chemical properties, and that there is such a large amount, more than 30 per cent., of the isotope in the mixture. Imagine that we have a mixture of what we might call light chlorine and heavy chlorine. The molecules of the light chlorine will, on the average, have a greater velocity than those of the heavy. Thus, if we consider a reaction such as that between chlorine and arsenic, or between hydrochloric acid and an alkali, a larger proportion of the faster molecules than of the heavier ones would strike against the absorbing substances and be absorbed, so that the gas left behind would gradually increase in density. I have calculated the kind of increase that you would get from an effect of this kind. I took the case of hydrochloric acid rather than that of chlorine, because, supposing there are two chlorines, you can only get two hydrochloric acid molecules, but you could get three different molecules of chlorine; and the case is made a little simpler by dealing with hydrochloric acid rather than with chlorine. The result of my calculation is, that if you start with a given volume of HCl, and wish to make an alteration of one part in a thousand in the density, you would have to reduce the volume to 37 per cent. of its original value. If you wished to produce an alteration of $\frac{1}{2}$ per cent. in the density, you would have to carry the reduction of the volume to about 1/180 of the original value, so that you would have to reduce a litre to about 5½ c.c. If you wished to produce a change of 1 per cent., you would have to reduce the volume to about 1/24,000th part of its original value, and so you would have to leave only about 0·04 c.c. of your litre. But considering the fact that the atomic weight of chlorine has been determined by many people to one part in a thousand, it would seem that it ought not to be a very difficult matter to detect a change of ½ per cent. in the atomic weight. So that it seems to me that an experiment which apparently does not present any prohibitive difficulties—though you never can be sure until you start these things—would enable one definitely to settle the question whether chlorine was a mixture or not. If I am right, there are certain processes by which one could fairly easily alter the density of chlorine. The question arises whether those chemists who have determined the atomic weight of chlorine have gone through processes anything resembling the one I have just sketched. I do not see that there is any evidence that in their determination they in any way approached to such a method of selection as that which I have suggested, so that, if the different chemists had been supplied with chlorine of the same composition, I think that they would have got by the methods they employed results for the atomic weights which were concordant to one part in a thousand. Then the question arises, Is it likely that the various samples of chlorine should be of such invariable composition? This leads us to speculations about the early history of the world, the methods in which chlorides were formed, and other subjects on which our information is not very definite; but you will notice from what I have said that though, no doubt, you might have circumstances in which chlorine of abnormal density is produced, yet whenever this abnormal chlorine is produced, a very much greater amount of normal chlorine has to be absorbed along with it. For example, chlorine which had been altered by 1 per cent. would be only 1 part in 20,000 of the chlorine in the chloride that had been produced along with it. So that the chances of getting the abnormal specimen would be somewhat small. Then again you have to remember that probably chlorides have been in solution in the sea; this would tend to mix them up; how complete the mixing would be would depend on circumstances of which we have little or no knowledge. But I do not know whether it is very profitable to speculate on this point, because I think that the whole question could be settled by a comparatively simple experiment.

I consider that it is all the more desirable that it should be settled in this way, because the information that is derived from the positive ray method gives us no direct information about the chemical properties of the substances giving the two lines corresponding to the two isotopes. Two lines may always occur together without necessarily being due to isotopes. The heavier element may be a compound of the lighter, or the lighter may be due to the dissociation of the atom of the heavier; or again it may be that the introduction of a substance like chlorine produced a kind of catalytic effect, and led to the formation of compounds which did not necessarily contain chlorine at all. The evidence as to the chemical properties which we derive from the study of the positive rays is very indirect, and it is highly desirable that some direct experiment should be made. If we take, for example, two substances found by Mr. Aston—35 and 37—we might imagine that the 37 was a compound of chlorine with two atoms of hydrogen. I know that the chemist would treat with derision a compound with that composition; so should I, if the hydride was formed under normal circumstances; but what I think is not sufficiently recognised is that the chemical properties of charged atoms—and it is charged atoms that occur in the discharge tube—are probably very different from those of uncharged ones. For example, we regard the normal chlorine atom as having seven electrons in the outer layer, and as being able, therefore, to take one hydrogen before it becomes saturated. Now if the chlorine atom becomes positively electrified, it loses an electron, and has only six in the outer layer; it is now analogous to the normal atom of oxygen, and can take up two atoms of hydrogen before being saturated, and form the compound H_2Cl. Or to take the case of oxygen, whose normal atom has six electrons in the outer layer and has room for two hydrogens; when positively electrified, it has only five electrons and has room for three hydrogens, and so can form the compound H_3O, with a molecular weight of 19. As a matter of fact, we do very often find, on the positive ray photographs, lines with an atomic weight of 19.

In passing I might mention that I think it is by no means impossible that the inert gases might, in the discharge tube, be able to form compounds. For example, neon has an outer layer of eight, but if it becomes positively electrified the eight is reduced to seven, and there is room for an atom of hydrogen, so that it is possible, though I do not say it is very probable, that neon may, in a discharge tube, form a hydride.

The behaviour of electrified atoms as distinct from normal atoms would seem to be well worthy the attention of chemists, and I think would yield interesting results. We are not helpless in the positive ray method with regard to telling whether a substance is a molecule or an atom, because there are, in general, well-marked distinctions which mark the two classes of particles. If a line is due to an atom then we generally find another line due to the atom with a double charge. It is very much rarer to find a molecule with a double charge. It is very much rarer—but that rule is not without exception—there are molecules with double charges. Another test is that when we find a positively electrified atom, in many cases we find a negatively electrified one. We do not by any means so frequently find a negatively-electrified molecule, but then again this also is a rule which is not by any means without exception. My experiments with unsaturated molecules—and I include under that term those which contain what the chemists call double bonds—show that they can, under suitable circumstances, require a double charge. Well, Mr. Aston has applied all these tests to the line corresponding to the atomic weight 37, and he finds it has a double charge; he finds also it occurs on the negative side; so it passes all tests we can apply to distinguish between a molecule and an atom, and there is thus a strong presumption that it is due to an element. But then again there is another test which I am not so sure it has passed quite so successfully. If chlorine is an invariable mixture of these two components, and if these two components are associated so closely with each other that they cannot be separated by ordinary chemical methods, then we should expect that under all circumstances the ratio of the intensities of the lines should be invariable, and should have a value which would correspond to that which would account for the abnormal atomic weight of the mixture. Some few years ago I made a large number of experiments on chlorine by the positive ray method, trying to find if the large departure of the atomic weight of chlorine from an integer was due to its being a mixture. My arrangement was by no means so accurate as Mr. Aston's, and I was not able to determine with any certainty the atomic weight, but I found the line at 37 and at first thought it was an element; the reason I gave up that assumption was that I found the proportion between the intensity of this line and that of the chlorine line was exceedingly variable. In some photographs the two were comparable in intensity; in others one was very faint compared with the other, and I could not find the 37 line at all on the negative side. So I gave up the idea that it was a separate element. I quite admit that the evidence in favour of it being an element has been raised to quite another plane by Mr. Aston's discovery of the atomic weight. That, of course, introduces—if the atomic weight is 35—a difficulty which was left entirely unexplained by my supposition about hydrides. But even yet I do not understand why I got this very large variation in the intensities, and from what I can see from Mr. Aston's paper in the 'Philosophical Magazine,' it seems to me that in the photograph there are larger variations than one would expect if the two chlorines were mixed in invariable proportion, and if their properties were practically identical. I do not mean to urge this as anything serious, but it does leave yet something to be explained, namely, how these two substances, supposed to be in invariable proportions and to have the same properties, can give rise to different ratios in the intensities of their lines.

Finally, a very interesting and important result—one which is fundamental on any theory of the ultimate constitution of matter—is that all the atomic weights which Mr. Aston has determined are integers, within the limits of his experimental error. That is a result of enormous importance. Its importance depends to a peculiar extent on the accuracy to which we can carry the determination of the atomic weight. I may perhaps illustrate my point in this way: If the atomic weight of chlorine is exactly 35, then if the atom is built up of three hydrogen atoms and eight helium ones, assuming the atomic weight of helium to be 4 and that of hydrogen 1·008, there would be a loss of mass, and therefore a liberation of energy when the chlorine atom is formed. If, on the other hand, the atomic weight of chlorine were greater than 35·024, there would be a gain of weight and an absorption of energy. Thus, an accuracy of 1 part in 2000 in the determination of the atomic weight of chlorine would be required to settle whether the formation of the chlorine atom was accompanied by an absorption or liberation of energy. Now, though I have long advocated the determination of atomic weights by positive rays, I do not think that just at present we can claim an accuracy of one part in a thousand; and, from some points of view, the focus method which Mr. Aston uses is, I think, more liable to error than the older method. One reason for this is that the quantity which Mr. Aston has to measure is the position of the edge and not the middle of a line; and one feature of the photographs of the positive rays is the way that the lines broaden when the exposure is increased. A line which looks like a spider line for a short exposure may under exactly similar circumstances become quite thick when the time of exposure is increased. Now, if you are going to measure an atomic weight to one part in a thousand, and do it step by step, starting from hydrogen, supposing the two lines corresponding to successive steps are 5 mm. apart, you will have to measure to 1/200th of a millimetre. I am very doubtful whether, when you are dealing with lines of different intensities, you can trust your measurements of the edges of these lines to anything like 1/200th part of a millimetre. In the other method, a spreading of the lines would not be so important if the thickening were symmetrical.

There is just one other point which I may illustrate by taking the case which in principle is identical with Mr. Aston's method. Suppose a horizontal beam of positive rays is deflected downwards by an electrostatic field concentrated at A, and upwards by a magnetic field concentrated at B. Then, if v is the velocity of the rays, the vertical deflection $y = \text{PN}$ at a point, P, will be given to a first approximation by the equation

$$y = -\frac{\alpha e}{mv^2}(x+a)+\frac{\beta e}{mv}x, \tag{1}$$

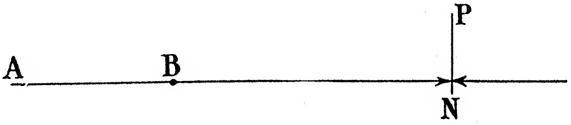

Fig. 1.

where α and β are constants depending on the electric and magnetic fields respectively; $x = \text{BN}$, $x+a = \text{AN}$. The rays corresponding to different values of v form a beam, and this beam will have a bright edge, a caustic, where consecutive rays intersect. At a point on this caustic the differential of 1 with respect to v must vanish, so that

$$2\frac{\alpha e}{mv^3}(x+a)-\frac{\beta e}{mv^2}x = 0,$$

or

$$v = \frac{2\alpha}{\beta}\left(\frac{x+a}{x}\right). \tag{2}$$

Substituting this value in (1) we see that

$$y = \tfrac{1}{4}\frac{\beta^2}{\alpha}\frac{x^2}{x+a}\frac{e}{m} \tag{3}$$

is the equation to the caustic.

The caustic is thus a hyperbola passing through B; one asymptote is parallel to $y = \frac{1}{4}\frac{\beta^2 e}{\alpha m}x$, the other to $x = 0$. The particles corresponding to the different atoms and molecules in the positive rays would have different hyperbolic caustics, and if these rays fell on a photographic plate, PQ, a series of images would be formed. As, however, each point on the caustic corresponds to a special value of v, the formation of these images requires the positive rays to contain particles with the appropriate velocity. This velocity is given

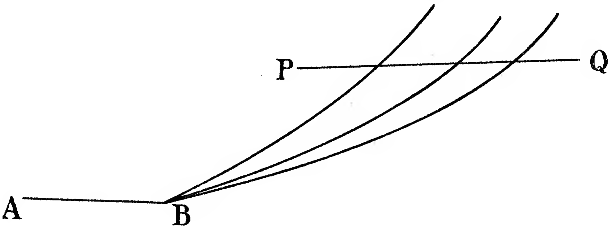

Fig. 2.

by equation (2), and we see that when x is large compared with a the velocity is $2\alpha/\beta$ and is the same for all particles. If the photographic plate is placed at right angles to the path of the undeflected rays, x is constant over the plate; hence by equation (2) all the rays that come to a focus on the plate must have the same velocity. If there are no particles belonging to a particular element with this velocity, the image corresponding to that element will be out of focus. We see from (3) that the deflections of the image will be inversely proportional to the atomic weight.

If the rays corresponding to each element only include a small range of velocities, then the photographic plate must be inclined so as to cut the caustics at points corresponding to those velocities. If, as in Mr. Aston's experiments, mv^2 is constant, then we have from equation (2)

$$\frac{4m\alpha^2}{\beta^2}\left(\frac{x+a}{x}\right)^2 = \mathrm{C};$$

combining this with (3) we see that

$$y = e\,\frac{\alpha}{\mathrm{C}}\,(x+a)$$

is the equation to the line for the photographic plate.

Thus the plate must pass through the point A. The distance, d, of the image due to a mass, m, from A, measured along the plate, is given by

$$\frac{md^2}{(d-a)^2} = \text{constant.}$$

This is far from a linear relation, so that interpolation to find the value of m for a particle giving an image between those of two particles of known masses would, without elaborate corrections, lead to results which might differ appreciably from the true values.

It would probably be only a small thing, but it would be a thing which I think would have to be taken into account in dealing with an accuracy of 1 part in 1000; but Mr. Aston has shown such great ingenuity in overcoming other difficulties that I feel no doubt that he will be successful in rendering his method free from the objection.

I have only one other word to say, and that is that this is a very striking example of the results which flow from the application of physical methods to chemistry. It is not the first case. We had the case of argon; we had the case of the structure of crystals; and I am quite sure that it will not be the last. I believe there is no branch of science where promise of great discoveries is more hopeful than those which will result by researches which involve the application of physical principles and physical measurements to chemical phenomena.

DR. F. W. ASTON: In the very short time at my command, I shall be unable to describe my apparatus, which is rather unfortunate, as several of the objections raised by the first speaker rather depend upon it. But I will deal with the points in the order in which Sir Joseph Thomson raised them. As regards the experiment suggested for the separation of hydrochloric acid, I think there is every probability of its working, if carried out under reasonable conditions. As far as I know, the mathematics of the experiment would be much the same as those in diffusions through pipeclay, the method I used in the case of the isotopes of neon, and in that case a positive separation appears to have been obtained. I obtained a difference of density —between the lightest and the heaviest sample of neon—of 0·7 per cent., which, I think, was real. As regards the addition of hydrogen to charged atoms, I presume Sir Joseph Thomson means that, if there was an atom of chlorine exactly 35·0—supposing my figures to be correct—then the other lines—the lines that one gets at 36, 37, and 38—would be due to hydrogen addition products, and that a charged chlorine might be capable of taking on one more hydrogen than an uncharged one. This is certainly a very interesting possibility, but I think it is rather discounted by the fact that if that were so, if the charged particle can take up one more hydrogen, the charged atoms of the inactive gases certainly ought to take up one hydrogen. I have seen no general indication of such hydrides, although they may be there, though too faint to be seen. But that, of course, does not get round the chemical atomic weight, because, if the fundamental chlorine is 35, it seems quite impossible to account for the chemist's atomic weight of 35·46. One must have a mixture of heavier atoms mixed with the 35 to account for that. The ratio of the intensity of the lines would be best determined by electrical methods; the photographic method is obviously a dangerous one to use for numerical values. One can certainly say that one isotope is there in greater proportion than another if its line is darker, because isotopes must have the same effect on the photographic plate; but the exact proportion is, of course, a matter that depends on the mechanism of the photography,* and therefore one cannot put too much value on the relative intensities of a plate. If one takes what seems a reasonable range of intensity, I think, with regard to the isotopes I have so far determined, their intensity corresponds very well with the actual chemical atomic weight when that is known with great certainty, as in the case of chlorine.

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* The positive rays do not penetrate the photographic film to any appreciable extent, so that their action is not really comparable to that of light. Hence the photometric laws established for the latter will not hold in general for the purely surface effect of positive rays, though they may be approximately similar over a limited range of intensity.

[A slide was then shown of the mass spectra of chlorine, and it was indicated that a large number of lines of known mass were available with which to compare the chlorine lines. Also that the evidence was quite uncompromising both as regards the absence of a line 35·46 and the presence of a group of lines of integral mass 35, 36, 37, 38, as due to the presence of chlorine in the discharge tube.]

I have recently obtained conclusive proof from negatively charged lines, which only appear at 35 and 37, that these are the elementary lines of chlorine, 36 and 38 being hydrochloric acid.

In the matter of accuracy of measurement, I think Sir Joseph Thomson is mistaken when he says I should have to measure to 1/200th of a millimetre to get an accuracy of 1 part in 1000. The actual distance apart of two lines, say for simplicity 10 and 11, differing by 10 per cent., is about 1 cm.; hence, to compare masses to 1 part in 1000, it is only necessary to measure to one-tenth of a millimetre.

In my first experiments with neon I used the most diffracted edge of the line, as that seemed to give the most reliable results; since then the focus has been much improved, and the lines are wedge-shaped similar figures, so that one can check the results by measuring from both edges or from the middle. I admit that edge measurement should only be relied upon in the case of lines of approximately the same intensity; in that case there seems no objection to it.

[A slide was then shown of a recent analysis of rays of the element lithium, generated by means of a heated anode, which gave parabolas, clearly indicating the presence of isotopes 6 and 7.]

[Referring to a slide of the most recent mass spectra of krypton and xenon]:—Here is the xenon group, which consists of five isotopes, possibly of seven. One can see five distinctly. That is the krypton group of six lines, and here is the mercury complex, which probably consists of six lines, ending with 202 and 204. You will note that, if the hydride explanation for this group was adopted, it would be necessary for mercury to take on a very large number of hydrogen atoms, and to do so in such a way that the compounds were invariably there in the same proportion, not only in the singly charged or first order lines, but also in the second, third, fourth, and higher orders.

The lowest spectrum is that of iodine: it shows a single line at 127. Iodine is a simple element: it has no isotopes.

This is a diagram showing the relation between the isotopes of the halogen elements and those of the inactive gases. You will note that no two occupy the same number on the mass scale. If they did, they would be isobares, as described by Prof. Soddy, of the same atomic weight, but of different chemical properties. I have not found any so far, but they must exist, as otherwise there do not seem to be enough whole numbers to go round.

[Other slides of mass spectra, and a list of the isotopes so far determined, were exhibited. The principle by which rays of the desired energy were selected by a diaphragm was explained, and the close analogy with the optical spectrograph indicated. The speaker was under some misunderstanding in connection with a point raised by Sir Joseph Thomson concerning the velocity of the rays. It was a second order effect in the caustic giving the focus; it does not appear likely to affect the present measurements to 1 part in 1000.]

Prof. F. SODDY: I wish to confine my remarks mainly to the early history of this subject which had its origin, of course, in the study of radioactive change. By 1910 it had been recognised that elements identical in chemical character existed, and the question was one really of the courage of the investigator in pushing his facts to their logical conclusion. My own mind, as to the complete chemical identity of certain elements encountered in the study of radioactive change, was made up after an investigation of the chemical properties of mesothorium and radium. I submitted a mixture of these two elements to a prolonged fractional crystallisation without altering the proportions of the mixture to the smallest extent. But there were numerous previously known examples—ionium and thorium worked out by Boltwood, and radium-D, and lead—though no one probably before thought such elements were really completely identical in chemical character, but merely that they must be very much alike. An important philosophical implication followed from the view of their complete chemical identity. For if ionium and thorium are as like as, say, one piece of lead is to another piece of lead, then is one piece of lead the same as another piece of lead? What real test has the chemist of the homogeneity of the elements? None! For all the tests of the chemist are chemical and he rarely, if ever, makes practical use of such old methods as diffusion, not to speak of the new methods we have been hearing about, which would suffice to reveal differences of atomic mass in elements of identical chemical character. As far back as 1910 I summed up the situation that has been reached in my Annual Report on Radioactivity to the Chemical Society:—

"The recognition that elements of different atomic mass may possess identical chemical properties seems destined to have its most important application in the region of inactive elements, where the absence of a second radioactive nature totally unconnected with the chemical nature makes it impossible for chemical identities to be individually detected. Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several of different atomic weights, or that any atomic weight is not merely a mean number . . . The absence of simple numerical relationships between the atomic weights becomes a matter of course rather than of surprise."

The results we have been listening to on the application of the positive rays to this question, first by Sir Joseph Thomson by the parabola method, and later, by Mr. Aston to a much greater degree of refinement, bear out the philosophical implication drawn in 1910 very thoroughly. The existence of what are now called isotopes was clearly recognised much earlier than the interpretation of them expressed by their name, which dates from 1913. The extensive researches of Dr. Fleck in Glasgow on the chemical character of all the products of radioactive change enabled the complete law of radioactive change of A. S. Russell, K. Fajans and myself to be formulated. Expulsion from the radio-element of an α-particle, carrying two positive atomic charges, causes the element to shift two places in the periodic table in the direction of diminishing mass and the expulsion of a β-ray or negative electron one place in the opposite direction. By one α- and two β-ray changes in succession the element reverts to its former place and, in this event, though the first and second products are necessarily chemically different from the parent, the third is necessarily identical with the parent. Moreover, the means of detection in this case gives the means of separation. For, if the sequence of one α- and two β-changes is represented $A \rightarrow B \rightarrow C \rightarrow D$, where where A and D are necessarily chemically identical and different from B and C, B and C may be separated chemically from A and D, and in course of time will generate D free from A, so that D can by a second separation be obtained alone. This double separation, a suitable interval elapsing between the two separations, is a common method of separating isotopes genetically connected. For example, radiothorium free from its isotope thorium is so obtained commercially from thorium minerals by separating the mesothorium and leaving it to grow fresh radiothorium after separation. There is no other way of separating it.

Writing a book in 1913 on the chemistry of the radio-elements I got tired of writing "elements chemically identical and non-separable by chemical methods" and coined the name *isotope*, signifying the same place, to express their nature in the light of the new interpretation of the periodic law. It was clear that the "places" of the latter expressed unit difference of charge in the atomic constitution, a conception which the researches of Moseley, on the wave-lengths of characteristic X-rays, later extended throughout the whole table. The nuclear theory of atomic structure of Sir Ernest Rutherford dovetailed in nicely. The α- and β-rays being expelled from the central nucleus of the atom, the expulsion of one α- and two β-rays leaves the *nett* nuclear charge and the whole external electronic system unchanged. Isotopes are, thus, elements with atoms made up of identical external systems and nuclei with the same *nett* charge. The constitution of the nucleus and the absolute number of contained + and − charges are different, but these differences are without effect on the chemical character.

The correctness of these views received very powerful support from the study of the atomic weight of lead derived from radioactive minerals. Both the uranium and thorium disintegrations end with the place in the periodic table occupied by lead, but whereas common lead has an atomic weight 207·2, that from uranium (atomic weight 238), formed by the successive expulsion of eight α-particles or helium atoms, should be 206 and that for thorium (atomic weight 232) by five α-particles, should be 208. The atomic weight of lead from the purest uranium minerals has been found to be 206·05 and from the purest thorium minerals 207·9. Moreover, thorium separated from uranium minerals contains the isotope ionium, 2 units less in atomic weight. Hönigschmid found, for a thorium preparation weighing a few grammes separated from 30 tons of Joachimsthal pitchblende by von Welsbach, an atomic weight 231·51 as compared with 232·12 for a pure preparation of ordinary thorium. The spectra of the two were identical and showed a complete absence of all impurities. This is one of the finest examples of the extent to which the complete chemical identity of isotopes has been experimentally established.

The results we have been listening to have shown what a powerful new weapon has been developed for the detection of isotopes among common elements not in actual course of change. Sir Joseph Thomson alluded to chlorine as the most dramatic example of isotopes, but, personally, I consider the discovery of metaneon, an isotope of neon, by himself and Mr. Aston, deserves that title. Coming in 1913, just as the theory of the radioactive isotopes had been eludicated, it constituted a most striking and suggestive confirmation, in a region of the periodic table remote from that in which the conception originated.

With regard to the interesting point raised by Sir Joseph Thomson, that the diameter of the outer atomic shell, though not the number of the electrons contained therein, may be affected by the gross charge of the nucleus, the nett charge being the same, so far as we can tell it is not. There is no trace of such an effect as you have—as in the example to which he referred, carbon and silicon—between two members of the same family. The atomic volumes of the two kinds of lead referred to are the same. I actually determined the atomic weight of my thorium lead from the density, on the assumption that the atomic volume was the same as that of ordinary lead, and got the value 207·74. A single chemical determination gave the value 207·69, and, in a more complete investigation, Hönigschmid, in Vienna, with another fraction of the same lead, found 207·77 (±0·014). T. W. Richards and Wadsworth have since found that the atomic volume of uranium lead of atomic weight 206·085 is the same as that of ordinary lead.

As regards the method suggested by Sir Joseph Thomson for the separation of the isotopes of chlorine by allowing hydrochloric acid to be absorbed by alkali, as a chemist I would differ from Mr. Aston's opinion that it would be analogous to the diffusion method which he has used in an attempt to separate the isotopes of neon, because, as a matter of fact, we have no conception as to why one element combines with another. It certainly has little to do with molecular speed, as the temperature coefficient of chemical change shows.

Sir JOSEPH THOMSON: I think you misunderstood me. I did not say there was any peculiarity in the affinity, so to speak, between the surface and the chemical. But the mere fact that some molecules were moving faster would cause them to strike oftener.

Prof. SODDY: Then this brings it down to the ordinary diffusion effect, which has been tried for neon and metaneon with somewhat divergent results.

I think Mr. Aston is to be very much congratulated upon the outcome of what is probably one of the most brilliant combinations of mathematical analysis and experimental skill this century has produced. I do not think chemists have any reason to doubt the accuracy, to one part in a thousand, which he claims for his determinations. He has on his plates a great range of thoroughly standard lines on which to test the accuracy, and I am prepared to accept his results as of the same order of approximation as is attained in the best chemical atomic weight methods.

Isotopes have been of the utmost use to chemists in the laboratory in various ways. Their use as indicators, developed by Paneth and von Hevesey, has enabled, for example, the solubility of very sparingly soluble salts of lead to be determined with ease. By their aid it has been possible to test the Nernst theory of E.M.F. at concentrations of the order of 10^{-9}, completely beyond the range of ordinary methods. Recently they have given practically a direct demonstration of the separated existence of the ions in an electrolyte. Thus, if ordinary lead chloride and a lead nitrate that has been "activated" by addition of thorium-B, an isotope of lead, are mixed in pyridine solution, the lead chloride crystallising is half as active as the original lead nitrate. But if, instead of being mixed with a salt that is ionised in solution, an active lead salt is mixed with inactive lead tetraphenyl, in a suitable solvent, the latter is found to be inactive when again separated. By the use of the same isotope the rate of self-diffusion of lead molecules through lead molecules has recently been experimentally measured.

Lastly, the existence of isotopes seems to offer in some cases a searching test of chemical logic,—but I have already taken more than I should of the time of the meeting.

Prof. T. R. MERTON: The most recent results of Dr. Aston and Mr. Thomson relating to the two isotopes of lithium provide a case in which a spectroscopic test can be applied more easily than in the case of any other isotopes. It is one of the greatest successes of Bohr's theory that the difference between the wave-lengths of the hydrogen lines of the Balmer series and alternate members of the ζ Puppis series of helium can be accounted for by the difference in the masses of the nuclei, and this can be applied in the same way to the two isotopes of lithium, of atomic weight 6 and 7. The structure of the red lithium line of wave-length 6708 A. has been investigated by several observers, and under normal circumstances consists of a doublet with a difference in wave-length of 0·151 A., the violet component being the stronger member. Now the doublet due to one isotope should be separated from the doublet due to the other by a difference in wave-length which can be calculated on exactly the same basis as in the case of the Balmer hydrogen lines and the lines of the ζ Puppis series; and if that is done, we find that the one doublet is displaced from the other by 0·087 A., and from the accepted atomic weight of lithium, 6·94, one doublet would presumably be about one-sixteenth of the intensity of the other. This is, from a photometric point of view, not a very great difference in intensity, three magnitudes only, and the displaced component should easily be visible. I am re-examining the lithium spectrum under a very high dispersion, and though the results are not yet complete, I have so far not been able to find any evidence of these faint components, and I think that if they are present at all, they must be very much less than one-sixteenth of the intensity of the main doublet. Some time ago, Prof. Lindemann and I tried experiments of the same kind with neon; in this case the difference between the two components should be much smaller, and on account of the physical widths of the lines, it was impossible to reach any conclusion, but the experiment will be repeated at the temperature of liquid hydrogen, and this should yield definite results.

A short time ago, General Hartley and I suggested a photochemical method of separating the isotopes of chlorine, but this method has not so far been successful. I have made some experiments on a method of separating possible isotopes of zinc. If zinc consists of two isotopes, as presumably it does, from the fractional value of its atomic weight, and if there is even a very small difference in the electrical properties of these two isotopes, it seemed possible that if a small quantity of zinc were kept fused for a long time under a large quantity of fused zinc chloride, there might be a settling-out of one of the isotopes into the small quantity of zinc; and although this investigation is not really finished, neither the densities nor the atomic weights having been determined, the spectra of the zinc treated in this way and of ordinary zinc appear to be identical to a very high degree of accuracy. The results for lead and thallium have already been published, and they show a perfectly definite difference in wave-length, which is in very close agreement in the case of uranium lead with the results obtained by Harkins and Aronberg in America. These differences are greater than would be expected from theory, but the lead atom is presumably very complex, and no definite conclusion can at present be drawn from this result. The case of lithium appears to be more crucial.

Prof. F. A. Lindemann: The only point which has been raised so far to which I cannot agree is the statement that isotopes have identical chemical properties. That they are very similar is indubitable, but I think it may be shown generally that two substances of different atomic weight must be separable chemically in principle.

If K_p is the equilibrium constant in the law of mass action it may be shown that $\frac{\log K_{p_1}}{\log K_{p_2}} = RT \log \frac{p_2}{p_1}$. If the force acting upon an atom in a solid is $\phi(r)$, r being the distance of the neighbouring atoms,

$$\log p = + \int_r^{\infty} \frac{\phi(r)\,dr}{K_1 T} + \int^T \frac{dT}{K_2 T^2} \int^T \left[K_3 - f\left(\frac{\phi'(r)}{M}\right)\right] dT + i,$$

and since K_1, K_2, and K_3 are constants, K_{p_1} can only be equal to K_{p_2} at all temperatures, *i.e.*, the substance can only be inseparable, if

$$f\left(\frac{\phi'(r_1)}{M_1}\right) \equiv f\left(\frac{\phi'(r_2)}{M_2}\right) \quad \text{and} \quad \int_{r_1}^{\infty} \phi(r)\,dr \equiv \int_{r_2}^{\infty} \phi(r)\,dr.$$

Since $r_1 = r_2$, these equations cannot be rigorously fulfilled unless $M_1 = M_2$. The difference will be very small if the chemical constants are given by $\frac{3}{2} \log M -$constant, and if there is a Nullpunktsenergie. The failure so far to separate isotopes seems to me to be an argument in favour of these two assumptions.

It seems highly probable that isotopes of diatomic molecules such as Cl_2 should have different spectra. According to the usual view the frequency in band spectra is given by $\nu = \nu_0 + \frac{h}{8\pi^2 I}(n_1^2 - n_2^2) = \nu_0 + \frac{h}{8\pi^2 I}(\pm 2n+1)$ since $n_1 - n_2 = \pm 1$. Here the moment of inertia I is that of the molecule, *i.e.*, $I = \frac{M_1 M_2}{M_1 + M_2} r^2$, since the distance apart r is constant. In Cl_2 if M_1 and M_2 are thirty-five and thirty-seven times M_0, therefore the moment of inertia can have any of the three values

$$r^2 M_0 \frac{35}{2}, \qquad r^2 M_0 \frac{1295}{72} \quad \text{or} \quad r^2 M_0 \frac{37}{2}.$$

Hence any line should be accompanied by two others, the three frequencies being given by

$$\nu_1 = \nu_0 + (\pm 2n+1) \frac{h}{8\pi^2 r^2 M_0} \frac{2}{35},$$

$$\nu_2 = \nu_0 + (\pm 2n+1) \frac{h}{8\pi^2 r^2 M_0} \frac{72}{1295},$$

and

$$\nu_3 = \nu_0 + (\pm 2n+1) \frac{h}{8\pi^2 r^2 M_0} \frac{2}{37}.$$

Since $M_0 = 1{\cdot}65 \,.\, 10^{-24}$ and $r_0 < 3{\cdot}10^{-8}$, $\Delta\nu > (2n \pm 1) \,.\, 8{\cdot}6 \,.\, 10^7$, which for 5000 Å. amounts to $\Delta\lambda > 7{\cdot}10^{-4}(2n \pm 1)$ Å. In other words, the chlorine spectrum should consist of numerous triplets of constant intensity ratio.

It might be possible to separate isotopes electrolytically if, as seems likely, they have different migration velocities in solution. If an ion of mass M retains the fraction $\frac{M}{M+m}$ of its momentum on collision with a solvent molecule of mass m, the velocity component due to the field is given by

$$\left(V_1 + \frac{Ft}{M}\right)\frac{M}{M+m} = V_1 \quad \text{or} \quad V_1 = \frac{Ft}{m},$$

V_1 being the remnant velocity at the beginning of a free path, F the electric force, and t the time between collisions. The mean velocity of migration is therefore

$$V = V_1 + \frac{Ft}{2M} = Ft\,(1/m + 1/2M).$$

If the free path l is the same for different isotopes

$$t = \frac{l}{V_0} = \frac{l}{\sqrt{(3kT)}}\sqrt{(M)},$$

V_0 being the equipartition velocity of thermal agitation.

Hence the migration velocity

$$v = \frac{l}{2m\sqrt{(3k\mathrm{T})}} \cdot \frac{2\mathrm{M}+m}{\sqrt{(\mathrm{M})}} \quad \text{and} \quad 1/v\,\frac{dv}{dm} = \frac{1}{2\mathrm{M}} \cdot \frac{2\mathrm{M}-m}{2\mathrm{M}+m}.$$

For lithium, where M_1 and M_2 are 6 and 7 if $m = 18$, there should be a difference of 1·24 per cent. in the migration velocity. For chlorine with $\mathrm{M}_1 = 35$ and $\mathrm{M}_2 = 37$, it should be nearly 1·7 per cent. If a solution were electrolysed in some medium like gelatine, the head of the column should contain one isotope only, and it is hoped shortly to carry out experiments to test this. In the above calculation, of course, the effect of hydration and association have not been taken into account.

One other point to which it may be worth while to refer is the very small energy difference between atoms if their atomic weights approach whole numbers closely. Quite apart from positive rays, chemical evidence shows that the difference between the mass of one carbon atom and three helium atoms is so small that the energy difference cannot exceed $4{\cdot}5 \,.\, 10^{-7}$ ergs per atom, *i.e.*, about 1/30 of the energy of the average radioactive change. If this is true, it somewhat curtails the store of intra-atomic energy, which it is hoped will one day become available.

A Generalisation of Weyl's Theory of the Electromagnetic and Gravitational Fields.

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1. In the non-Euclidean geometry of Riemann, the metric is defined by certain quantities, $g_{\mu\nu}$, which are identified by Einstein with the potentials of the gravitational field. H. Weyl has shown that, on removing a rather artificial restriction in Riemann's geometry, the expression for the metric includes also terms which are identified with the four potentials of the electromagnetic field. I believe that Weyl's geometry, far-reaching though it is, yet suffers from an unnecessary and harmful restriction; and it is the object of this paper to develop a still more general theory.

In passing beyond Euclidean geometry, gravitation makes its appearance; in passing beyond Riemannian geometry, electromagnetic force appears; what remains to be gained by further generalisation? Clearly, the non-Maxwellian binding-forces which hold together an electron. But the problem of the electron must be difficult, and I cannot say whether the